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14. ABSTRACT
Here, the oxygen surface exchange coefficient (k) and film stress of porous La0.6Sr0.4FeO3-? (LSF64) thick films were measured between 275-400C and 275-700C, respectively, using a bilayer curvature measurement technique. Similar to bulk samples, the thick film stress magnitudes were close to zero. The magnitude and activation energy of the porous thick film k's were also consistent with low temperature extrapolations of large grained, bulk sample behavior. However, unlike large grained, bulk LSF64 samples that only exhibited measurable chemical stress above 525C, the fine grained, porous LSF64 thick films studied here exhibited measurable chemical stress over the

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Report Title

Final Report for the 9 month Army Research STIR Agreement Number W911NF1310404

ABSTRACT

Here, the oxygen surface exchange coefficient (k) and film stress of porous La0.6Sr0.4FeO3-? (LSF64) thick films were measured between 275-400C and 275-700C, respectively, using a bilayer curvature measurement technique. Similar to bulk samples, the thick film stress magnitudes were close to zero. The magnitude and activation energy of the porous thick film k's were also consistent with low temperature extrapolations of large grained, bulk sample behavior. However, unlike large grained, bulk LSF64 samples that only exhibited measurable chemical stress above 525C, the fine-grained, porous LSF64 thick films studied here exhibited measurable chemical stress over the complete range from 275 to 700C. Further, the porous thin films exhibited a kink in their Arrhenius chemical stress behavior (displaying activation energies of 0.07 eV below at 525C and 0.5 eV above at 525C), suggesting a distinct lattice-dominated chemical stress response above 525C and a distinct grain-boundary-dominated chemical stress response below 525C. This the first time the curvature relaxation method has been used to extract k's from a porous film, the first time simultaneous stress and oxygen surface exchange measurements have been collected on a low-stress sample, and the first time a temperature-induced transition from grain-boundary-dominated chemical expansion to lattice-dominated chemical expansion has been observed.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Yang, Q. and Nicholas, J.D. Porous Thick Film Low Temperature Lanthanum Strontium Ferrite Oxygen Surface Exchange Coefficient Measurements by Curvature Relaxation. 225th Meeting of the Electrochemical Society, Orlando, FL, (2014).

Number of Presentations: 1.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received		Paper
06/30/2014	1.00	Qing Yang, Jason Nicholas. Porous Thick Film Lanthanum Strontium Ferrite Stress and Oxygen Surface Exchange Bilayer Curvature Relaxation Measurements, Journal of the Electrochemical Society (06 2014)

TOTAL: **1**

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

As shown at http://www.grc.org/programs.aspx?year=2014&program=ceramics, Dr. Nicholas was invited to deliver a "Using Mechano-Chemical Coupling to Probe Oxygen Surface Exchange Coefficients" presentation at the Solid State Studies in Ceramics Gordon Research Conference.

As shown at http://www.fusion-conferences.com/conference5.php, Dr. Nicholas was invited to deliver a "Separate Grain Boundary and Bulk Response in the Stress and Oxygen Surface Exchange Behavior of Lanthanum Strontium Iron Oxide Films Measured by the Curvature Relaxation Technique" presentation at the Oxide Thin Films for Advanced Energy and Information Applications Conference.

Dr. Nicholas is serving as a Journal of the Electrochemical Society Guest Editor for a Focus Issue on “Mechano-Electro-Chemical Coupling in Energy Related Materials and Devices”. The Call for Papers for this Focus Issue is available at http://jes.ecsdl.org/site/focus_issues/jes_mec_coupling.xhtml.

Dr. Nicholas served as the lead organizer for a new, 50-abstract Symposium at the Spring 2014 Electrochemical Society Meeting on “Mechanical-Electrochemical Coupling in Energy Related Materials”. The Call for Papers for this symposium is available at https://www.egr.msu.edu/nicholasgroup/ECS_Call_for_Papers_S2014.pdf.

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Qing Yang	1.00	
Vasiliy Sharikov Bass	0.25	
FTE Equivalent:	**1.25**	
Total Number:	**2**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Dr. Jason Nicholas	0.10	
FTE Equivalent:	**0.10**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See attachment

Technology Transfer

Attachment

Final Report for the 9 month Army Research STIR Project Number W911NF1310404

Dr. Jason D. Nicholas

Michigan State University

https://www.egr.msu.edu/nicholasgroup/

Statement of the Problem Studied

The objective of the proposed work was to use the mechanical-electrochemical coupling accompanying ionic defect concentration changes in Mixed Ionic Electronic Conductors to probe and engineer ionic defect concentrations.

Summary of the Most Important Results

As shown in the attached submitted Journal of the Electrochemical Society article on "Porous Thick Film Lanthanum Strontium Ferrite Stress and Oxygen Surface Exchange Bilayer Curvature Relaxation Measurements",

- We used the mechano-chemical response of a porous thick film to measure that film's oxygen surface exchange coefficient for the first time
- We performed the world's first simultaneous stress and oxygen surface exchange measurements on a porous thick film material
- We demonstrated that the curvature relaxation technique developed by our group to measure oxygen surface exchange coefficients can be used to measure both dense and porous films.
- We measured oxygen surface exchange coefficients for the solid oxide fuel cell cathode material lanthanum strontium iron oxide below 400^{o}C for the first time (this oxygen surface exchange data will be important for the development of low temperature Solid Oxide Fuel Cells).
- We measured the free energies of formation for oxygen vacancies at the grain boundaries and the bulk of lanthanum strontium iron oxide for the first time.
- We showed how microstructure can impact mechano-chemical coupling by directly observing a temperature-induced transition from a grain-boundary-dominated chemical expansion regime to lattice-dominated chemical expansion region for the first time.

Originally Stated Project Goals

The objectives stated in the original proposal were to 1) demonstrate how a novel curvature relaxation method can be used to extract *in situ* oxygen surface exchange coefficients and elastic constants from porous catalyst thick films, and 2) use this new technique to evaluate the hypothesis that the oxygen surface exchange coefficient (k), equilibrium oxygen vacancy concentration (c_v), and catalytic activity (z), of gadolinium doped ceria (GDC, $Ce_{0.9}Gd_{0.1}O_{1.95-\delta}$) can be enhanced through the application of a biaxial tensile strain. The ability to tailor surface and/or bulk ionic defect concentrations and transport properties has important implications for catalysts, multilayered electronic devices, microelectronic mechanical systems, and other mission-critical army-devices. In this short, 9 month study, we were able to demonstrate that a novel curvature relaxation method can be used to extract *in situ* oxygen surface exchange coefficients from porous catalyst thick films, and we were able to observe new microstructurally controlled mechano-chemical coupling phenomena. It is hoped that with additional funding from the Army Research Office, we will be able to continue exploring the intriguing relationships between mechanics, microstructure, and electrochemistry.

Project Development History and Future Opportunities

Since the title of the proposed work was "Strain Engineering Defect Concentrations in Reduced Ceria for Improved Electro-Catalytic Performance" we started this work by producing gadolinium doped ceria thick films and then measuring them under low p_{O_2} atmospheres (where ceria becomes reduced). Unfortunately as shown in Fig. 1, using the 3D FIB-SEM reconstruction and curvature relaxation processes described in Yang and Nicholas[1] we quickly encountered the fact that our porous ceria films displayed oxygen surface exchange coefficients (*k's*) very different than those in the literature. Specifically, the measured porous GDC *k* values were 2 orders of magnitude lower than those reported for GDC thin films,[2,3] and 2-3 orders of magnitude lower than those reported for dense "bulk" GDC in the literature.[2,4,5] Recent conference proceeding data[6,7] has shown that the oxygen surface exchange coefficients of ceria are <u>extremely</u> sensitive to surface impurities, and it is therefore possible that impurities existing in the raw materials, introduced during powder processing, or diffusing to the film surface from the YSZ support during film sintering poisoned the GDC surface.

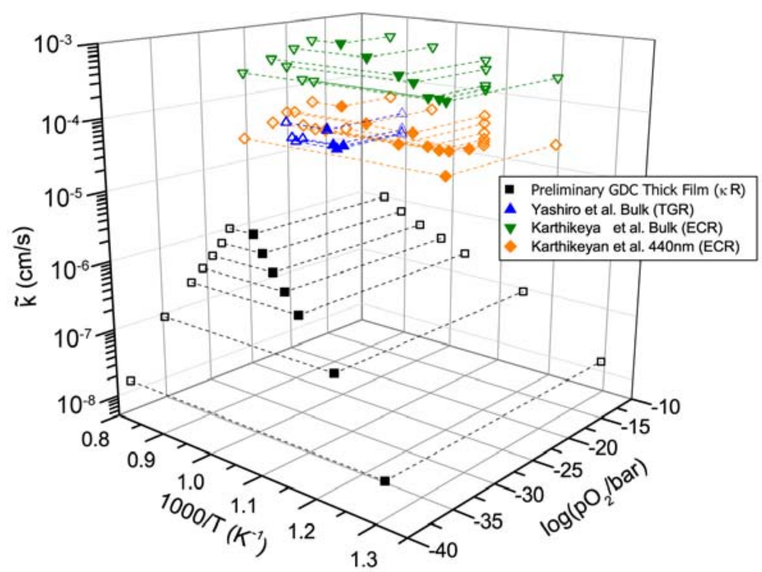

Fig. 1. *Oxidizing k values for porous ,2.1 μm thick 1050°C sintered GDC films on 100-oriented, 500 μm thick yttria stabilized zirconia single crystal wafers (black squares) compared with dense thin film GDC k values from the literature. The open symbols are projections onto the back walls.*

Because of the short 9-month duration of this project, and the fact that the first stated proposal objective was to determine if the curvature relaxation method could be used to measure *k's* in porous films (not investigate potential sources of GDC surface contamination), we chose to redo our experiments using lanthanum strontium ferrite (LSF) porous films. LSF was chosen because no reports showing that LSF is sensitive to small amounts of surface impurities exist in the literature, and because LSF is mechano-chemically active in air (greatly simplifying the experimental difficulty and removing p_{O_2} uncertainty as a potential source of error). That said, a full investigation into the relationship between surface impurities, *k,* grain size, stress, p_{O_2}, testing temperature, fabrication methods, and testing methods in ceria is still needed and would allow us to develop and understanding of how to engineer the electrochemical properties of ceria.

As summarized extensively in the attached submitted Journal of the Electrochemical Society article on "*Porous Thick Film Lanthanum Strontium Ferrite Stress and Oxygen Surface Exchange Bilayer Curvature Relaxation Measurements"* our experiments with porous LSF films were highly sucessful in terms of establishing the validity of the curvature relaxation technique, providing desperately-needed simulatneous, *in situ* LSF *k* and stress measurements as a function of temperature, and highlighting how microstructural effects can impact mechano-chemical coupling. Future work on LSF could focus on 1) rigorously establishing the microstructure − mechano-chemical coupling relationships in the LSF system, 2) examining how and why strain can be used to improve the electrochemical properites, 3) understanding how surface impurity, temperature, p_{O_2}, fabrication method, and testing method impact the measured *k*, and 4) using the observed relationships to produce improved materials for catalyst, fuel cell, and other applications.

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